



⑪ Publication number : **0 435 745 A1**

⑫ **EUROPEAN PATENT APPLICATION**

②① Application number : **90403671.2**

②② Date of filing : **19.12.90**

⑤① Int. Cl.<sup>5</sup> : **C10M 169/00, C10M 169/06, C10M 161/00, // (C10M169/00, 101:02, 115:08, 135:18, 137:10, 137:10, 143:02), (C10M169/06, 115:08, 135:18, 137:10, 137:10, 143:02), (C10M161/00, 135:18, 137:10, 137:10, 143:02), C10N10:04, C10N10:12**

③① Priority : **27.12.89 JP 336702/89**

④③ Date of publication of application : **03.07.91 Bulletin 91/27**

⑥④ Designated Contracting States : **DE FR GB**

⑦① Applicant : **NISSAN MOTOR COMPANY LIMITED**  
**No. 2, Takara-cho, Kanagawa-ku**  
**Yokohama-city, Kanagawa-prefecture (JP)**  
 Applicant : **Showa Shell Sekiyu Kabushiki Kaisha**  
**3-2-5, Kasumigaseki Chiyoda-ku**  
**Tokyo (JP)**

⑦② Inventor : **Abe, Saburo**  
**1701-3-12-404, Okada**  
**Atsugi-shi, Kanagawa 243 (JP)**

Inventor : **Asano, Hideo, Room No. 3-202**  
**NISSAN APART, 3-1, Tsujidounishikaigan**  
**Fujisawa-shi, Kanagawa 251 (JP)**  
 Inventor : **Watanabe, Iwao**  
**1-6-1-126, Hachimandai**  
**Isehara-shi, Kanagawa 259-11 (JP)**  
 Inventor : **Sakai, Takehisa, c/o SHOWA SHELL**  
**SEKIYU K. K.**  
**2-5, Kasumigaseki 3-chome**  
**Chiyoda-ku, Tokyo 100 (JP)**  
 Inventor : **Hasegawa, Ryo, c/o SHOWA SHELL**  
**SEKIYU K. K.**  
**2-5, Kasumigaseki 3-chome**  
**Chiyoda-ku, Tokyo 100 (JP)**  
 Inventor : **Goto, Humio, c/o SHOWA SHELL**  
**SEKIYU K. K.**  
**2-5, Kasumigaseki 3-chome**  
**Chiyoda-ku, Tokyo 100 (JP)**  
 Inventor : **Tajiri, Hiroshi, c/o SHOWA SHELL**  
**SEKIYU K. K.**  
**2-5, Kasumigaseki 3-chome**  
**Chiyoda-ku, Tokyo 100 (JP)**

⑦④ Representative : **Bourgognon, Jean-Marie et al**  
**Cabinet Flechner 22, Avenue de Friedland**  
**F-75008 Paris (FR)**

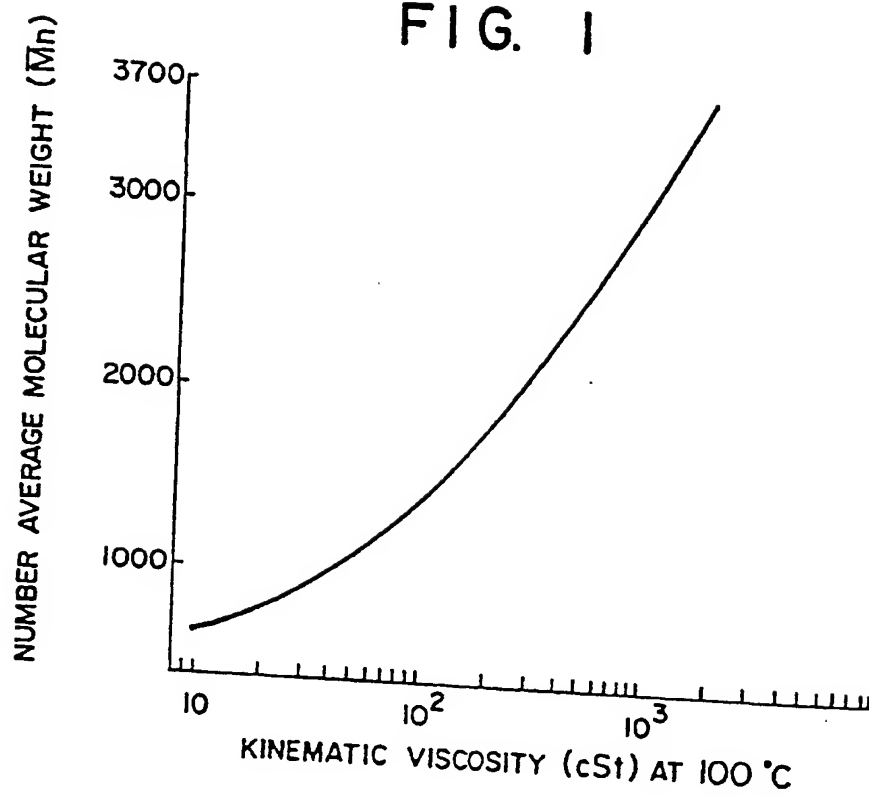
⑤④ **Grease for constant velocity joint.**

⑤⑦ A grease composition for constant velocity joints comprises a base grease comprising a mineral oil and an urea compound, to which are added the following compounds :

- (1) 0.5 - 5 % by weight, based on the grease composition, of a molybdenum dithiocarbamate compound and 0.5 - 5 % by weight, based on the grease composition, of a molybdenum dithiophosphate compound as organo-molybdenum compounds,
- (2) 0.5 - 10 % by weight, based on the grease composition, of zinc dithiophosphate compound as an extreme pressure agent, and
- (3) 0.5 - 60 % by weight, based on the grease composition, of a copolymer of ethylene and branched  $\alpha$ -olefin.

EP 0 435 745 A1

FIG. 1



## GREASE FOR CONSTANT VELOCITY JOINT

The present invention relates to greases for constant velocity joints, especially plunging type constant velocity joints.

Representatives of plunging type constant velocity joints include double offset type constant velocity joints (DOJ type) and tripod type constant velocity joints (TJ type).

Hitherto, as lubricants there have been used greases to which molybdenum disulfide, extreme pressure agents containing lead, sulfur-phosphorus extreme pressure agents or the like are added. However, cars equipped with double offset type constant velocity joints filled with these greases have the problems that beating noise or booming noise is generated or bodies vibrate at high speed driving. On the other hand, cars equipped with tripod type constant velocity joints have the problem that shudder of bodies occurs at acceleration. Further, plunging type constant velocity joints have far more sliding contact than shudder contact and when rotating torque is delivered with angles, axial force is generated by frictional resistance at sliding parts.

If a large amount of axial force is generated, vibration of bodies occurs to give discomfort to persons in the cars. Therefore, it is desirable to reduce axial force as much as possible.

Thus, in the case of plunging type constant velocity joints, lubricants are filled therein in order to reduce frictional resistance and to improve slidability.

As explained above, according to the conventional techniques, there have been developed no greases of low friction coefficient for inhibition of generation of beating noise or booming noise or occurrence of shudder of bodies at high speed driving or acceleration of speed in cars equipped with constant velocity joints, especially plunging type constant velocity joints.

According to the present invention, above problems have been solved by providing greases for constant velocity joints by adding diurea compounds, organic molybdenum compounds, extreme pressure agents and specific copolymers to base oils.

In the accompanying drawings,

Fig. 1 is a graph which shows relation between kinematic viscosity and molecular weight of copolymers.

Fig. 2 is a graph which shows relations among speed, axial force and sound pressure in the bodies of cars equipped with DOJ.

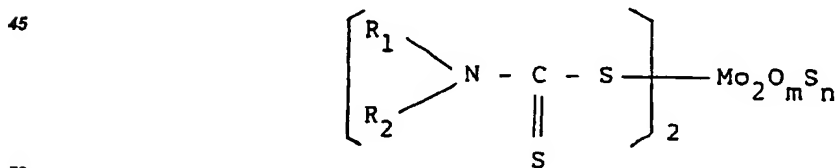
The present invention relates to a grease composition for constant velocity joints which comprises base greases comprising mineral oils and urea compounds and (1) 0.5 - 5 % by weight of molybdenum dithiocarbamate compounds and 0.5 - 5 % by weight of molybdenum dithiophosphate compounds as organic molybdenum compounds, (2) 0.5 - 10 % by weight of zinc dithiophosphate compounds as extreme pressure agents, and (3) 0.5 - 60 % by weight of copolymers having a molecular weight of 300 - 4,000 and comprising ethylene and branched  $\alpha$ -olefin.

The grease of the present invention may further contain antioxidants, oiliness agents, rust preventives and the like.

The base oils used in the present invention are mineral oil or synthetic hydrocarbon lubricating oils. As thickening agents, there may be used urea compounds (diurea compounds) which are superior in heat resistance to metallic soaps such as lithium soap.

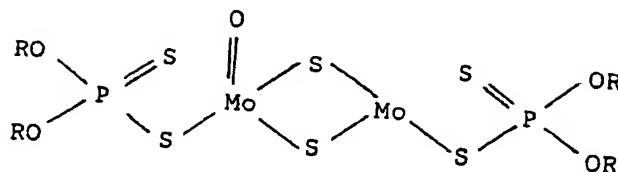
Organic molybdenum compounds used in the present invention comprise combination of molybdenum dialkyl dithiocarbamates and molybdenum dialkyl dithiophosphates or molybdenum diaryl dithiophosphates.

The said molybdenum dialkyl dithiocarbamates are represented by the following formula



wherein  $R_1, R_2$  each represents a  $C_1$ - $C_{24}$  alkyl group,  $m+n=4$ ,  $m=0-3$  and  $n=4-1$ .

The said molybdenum dialkyl dithiophosphates and molybdenum diaryl dithiophosphates are represented by the following formula

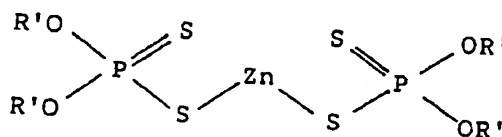


wherein R represents a primary or secondary alkyl group or aryl group.

When amounts of organic molybdenum compounds are too much, the effect does not increase but rather deteriorates. Thus, amounts of them are 0.5 - 5 % by weight, respectively and the total amount is 0.5 - 10 % by weight, preferably 2 - 5 % by weight.

Zinc compounds as an extreme pressure compound used in the present invention are zinc dialkyl dithiophosphate, zinc dialkyl dithiophosphate, or mixtures thereof.

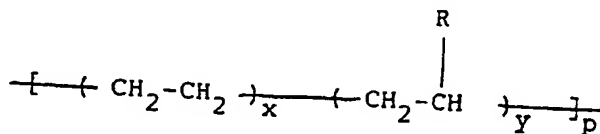
The said zinc dialkyl dithiophosphate and zinc dialkyl dithiophosphate are represented by the following formula



wherein R' represents a primary or secondary alkyl group or aryl group.

These organic zinc compounds as well as the above organic molybdenum compounds are very effective extreme pressure agents. Addition of too much amount of zinc compounds does not bring about further increase in effect but rather decrease, and hence an amount of the zinc compounds is 0.5 - 10 % by weight, preferably 0.5 - 5 % by weight.

The copolymers used in the present invention are oligomers of ethylene and branched  $\alpha$ -olefins and are represented by the formula :



wherein R represents a C<sub>1</sub>-C<sub>10</sub> alkyl group and x, y and p represent integers of 1-145, 1-95 and 1-60, respectively.

The above oligomers are synthetic oils of hydrocarbons having a molecular weight of 300 - 4,000 and free from polar groups and are effective for reducing axial force under low pressure.

Relation between viscosity and molecular weight of copolymers is as shown in Fig. 1. Addition of copolymers in a too much amount provides no further increase in effect but rather decrease and hence an addition amount is 0.5 - 60 % by weight, preferably 5 - 30 % by weight, more preferably 10 - 30 % by weight.

#### Comparative Example 1

A mixture of 90 % by weight of purified mineral oil (paraffinic base oil, viscosity index : 90 ; kinematic viscosities : 80.3 cst at 40 °C and 10 cst at 100 °C ; and pour-point : -17.5 °C) as a base grease and 10 % by weight of diurea compound was processed by a three-roll mill to obtain a grease composition. Properties of this composition, namely, consistency, dropping point, friction coefficient and axial force were measured and the results are shown in Table 1.

#### Comparative Example 2

A thorough mixture of a base grease comprising purified mineral oil (same as used in Comparative Example 1) as a base oil (83 % by weight) and a diurea compound (10 % by weight), and an organic molybdenum compound ① (molybdenum dialkyl(C<sub>1</sub>-C<sub>24</sub>) dithiocarbamate (4 % by weight), zinc dialkyl(primary and secondary alkyl) and diaryl dithiophosphate as an extreme pressure agent (2 % by weight) and octyldiphenylamine as an antioxidant (1 % by weight) was processed by a three-roll mill. Properties of the resulting grease composition were measured and the results are shown in Table 1.

### Comparative Example 3

Grease composition was obtained in the same manner as in Comparative Example 2 except that 2 % by weight of the organic molybdenum compound ① (molybdenum dialkyl(C<sub>1</sub>- C<sub>24</sub> alkyl) dithiocarbamate) and 2 % by weight of a molybdenum compound ② (molybdenum dialkyl(primary and secondary alkyl) and diaryl dithiophosphate) were used as organic molybdenum compounds. Properties of this composition were measured and the results are shown in Table 1.

### Example 1

To a base grease comprising 82 % by weight of purified mineral oil (same as used in Comparative Example 1) as a base oil and 10 % by weight of a diurea compound were added 1 % by weight of a copolymer (molecular weight : 3700) of ethylene and branched  $\alpha$ -olefin as oligomers, 2 % by weight of the organic molybdenum compound ① (same as in Comparative Example 2), 2 % by weight of the organic molybdenum compound ② (same as in Comparative Example 3), 2 % by weight of zinc dialkyl dithiophosphate as an extreme pressure agent, and 1 % by weight of octyldiphenylamine as an antioxidant. They were well mixed and then processed by a three-roll mill to obtain a grease composition. Properties of this composition measured are shown in Table 1.

### Examples 2 - 7

Grease compositions as shown in Table 1 were obtained in the same manner as in Example 1 except that amounts of the mineral oils and copolymers (molecular weight : 3700) of ethylene and branched  $\alpha$ -olefin as oligomers were changed. Properties of these compositions are shown in Table 1.

Comparison of the results of Comparative Example 3 with those of Examples 1 - 7 shows that the copolymers of ethylene and branched  $\alpha$ -olefins used in the present invention were added to greases of low friction coefficient, the low friction coefficient did not change, but axial force greatly decreased than greases of low friction coefficient which did not contain the copolymers of the present invention as shown in Table 1 and Fig. 2. It is considered that this is due to synergistic effect of addition of diurea compounds, organic molybdenum compounds, extreme pressure agents and copolymers.

Table 1

Items	Components (wt%)	Example							Comparative Example		
		1	2	3	4	5	6	7	1	2	3
Base grease	Mineral oil	82	81	78	73	63	53	23	90	83	83
	Diurea compound	10	10	10	10	10	10	10	10	10	10
	Oligomer	1	2	5	10	20	30	60	-	-	-
	Organic molybdenum compound ①	2	2	2	2	2	2	2	-	4	2
	Organic molybdenum compound ②	2	2	2	2	2	2	2	-	-	2
Additive	Extreme pressure agent ③	2	2	2	2	2	2	2	-	2	2
	Antioxidant ④	1	1	1	1	1	1	1	-	1	1
Con-sist-ency	Unworked	268	272	274	268	280	284	290	265	260	263
	Unworked 60 times	281	284	289	296	299	306	304	280	277	275
Properties	Dropping point °C	241	242	242	239	239	240	238	238	238	240
	Friction coefficient	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.10	0.03	0.03
	Axial force dB = 20 log (kg·f) ⑤	-3.2	-3.2	-3.4	-5.3	-7.0	-9.2	-7.9	1.7	-3.2	-3.2

(Note)

In Table 1, the oligomers are copolymers of ethylene and branched  $\alpha$ -olefins (molecular weight : 3700) ; the urea compounds are urea compounds mainly composed of diurea ; the organic molybdenum compounds ① are molybdenum dialkyl dithiocarbamates ; the organic molybdenum compounds ② are molybdenum dialkyl(primary and secondary) and diaryl dithiophosphates ; the extreme pressure agents ③ are zinc dialkyl(primary and secondary) and diaryl dithiophosphates ; and the anti-oxidants ④ are octyldiphenylamine.

Properties of grease compositions were measured by the following methods.

Consistency : JIS K2220 5.3

10 Dropping point : JIS K2220 5.4

Friction coefficient : ASTM D2266 (50 kgf x 600 rpm x room temperature x 15 minutes)

Axial force : by test on actual cars in which DOJ type constant velocity joints were mounted ;

$$dB = 20 \log (kg \cdot f)$$

15 Table 1 shows that the greases of the present invention have low friction coefficient and provide very low axial force.

As explained above, the greases of the present invention have low friction coefficient, are excellent in reducing axial force, can reduce discomfort for passengers and can provide comfortable driving environment.

## 20 Claims

1. A grease composition for constant velocity joint which comprises a base grease comprising a mineral oil and an urea compound and the following compounds ;

25 (1) 0.5 - 5 % by weight, based on the grease composition, of a molybdenum dithiocarbamate compound and 0.5 - 5 % by weight, based on the grease composition, of a molybdenum dithiophosphate compound as organic molybdenum compounds,

(2) 0.5 - 10 % by weight, based on the grease composition, of zinc dithiophosphate compound as an extreme pressure agent, and

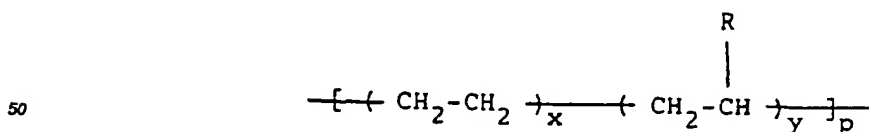
30 (3) 0.5 - 60 % by weight, based on the grease composition, of a copolymer of ethylene and branched  $\alpha$ -olefin.

2. A grease composition according to claim 1, wherein the molybdenum dithiocarbamate compound is molybdenum dialkyl dithiocarbamates.

35 3. A grease composition according to claim 1, wherein the molybdenum dithiophosphate compound is at least one compound selected from the group consisting of molybdenum dialkyl dithiophosphates and molybdenum diaryl dithiophosphates.

40 4. A grease composition according to claim 1, wherein the zinc dithiophosphate compound as an extreme pressure agent is at least one compound selected from the group consisting of zinc dialkyl dithiophosphates and zinc diaryl dithiophosphates.

45 5. A grease composition according to claim 1, wherein the copolymer of ethylene and branched  $\alpha$ -olefin is an oligomer of ethylene and branched  $\alpha$ -olefin which is represented by the formula :



wherein R represents an  $C_1$ - $C_{10}$  alkyl group and x, y and p represent an integer of 1 - 145, 1 - 95 and 1 - 60, respectively.

55 6. A grease composition according to claim 5, wherein the oligomer has a molecular weight of 300 - 4,000.

FIG. 1

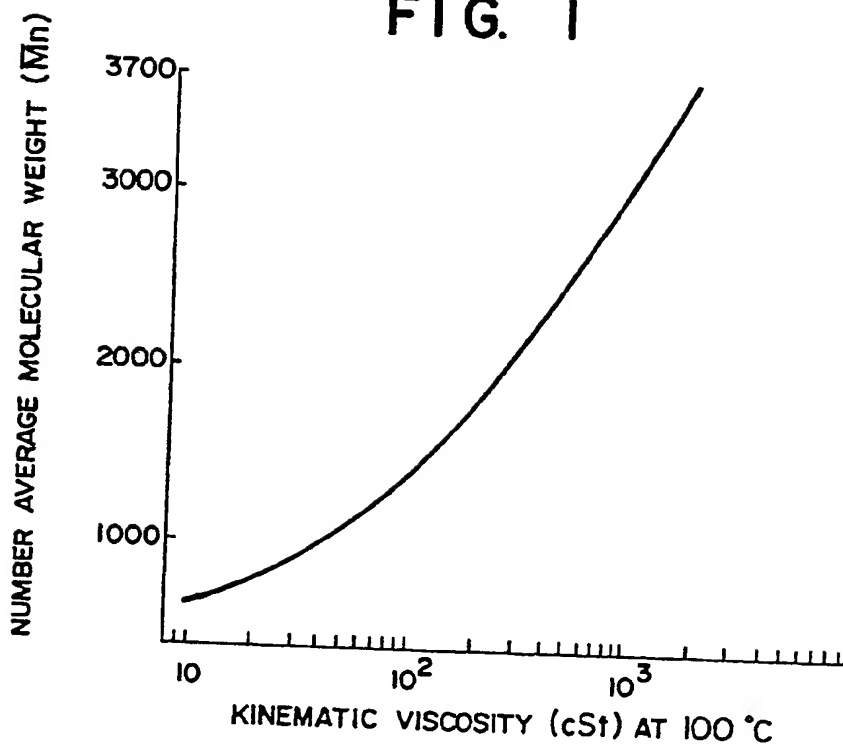
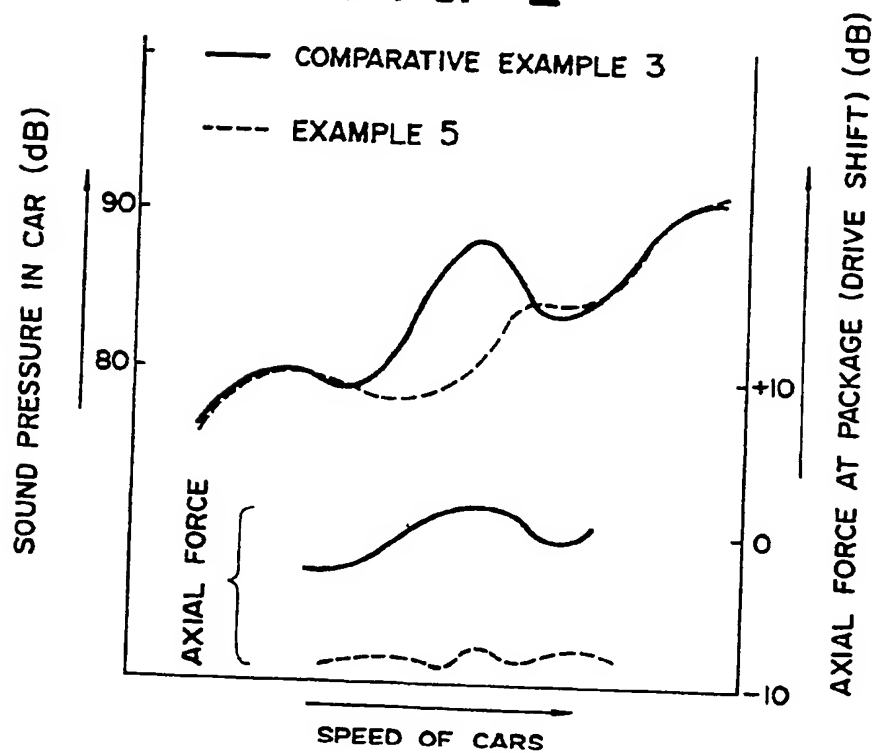


FIG. 2







European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 90 40 3671

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claims	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
A	GB-A-2 185 492 (NTN TOYO BEARING CO.) * Claims 6-12 *	1-4	C 10 M 169/00 C 10 M 169/06
P, A	WO-A-9 012 079 (AMOCO CORP.) * Page 6, line 24 - page 7, line 11; page 9, lines 18-22; page 47, lines 1-7 *	1,5	C 10 M 161/00 // (C 10 M 169/00 C 10 M 101:02 C 10 M 115:08 C 10 M 135:18 C 10 M 137:10 C 10 M 137:10 C 10 M 143:02 )
A	US-A-4 840 739 (S. MORI) * Column 2, lines 9-54 *	1,5	(C 10 M 169/06 C 10 M 115:08 C 10 M 135:18 C 10 M 137:10 C 10 M 137:10 C 10 M 143:02 )
A	DATABASE WPI, accession no. 77-20680y, Derwent Publications Ltd, London, GB; & JP-A-52 016 503 (CHUO YUKA) 07-02-1977 * Abstract *	1,5	(C 10 M 169/06 C 10 M 115:08 C 10 M 135:18 C 10 M 137:10 C 10 M 137:10 C 10 M 143:02 )
A	US-A-4 764 293 (J.C. ROOT)		(C 10 M 161/00 -/-
			TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
			C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-03-1991	Examiner HILGENGA K.J.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : oral-written disclosure F : intermediate document			

EPO FORM 1503 03.92 (P0401)



European Patent  
Office

# EUROPEAN SEARCH REPORT

Page 2

Application Number

EP 90 40 3671

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
			C 10 M 135:18 C 10 M 137:10 C 10 M 137:10 C 10 M 143:02 ) C 10 N 10:04 C 10 N 10:12 C 10 N 40:04 C 10 N 40:00 C 10 N 50:10
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	08-03-1991	HILGENA K.J.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 150 (02.91) (P0401)